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(54) Synthesis of metal matrix composites by transient liquid consolidation.

(57) A method is provided for fabricating metal matrix composites. Small diameter fibers, which may be in the form of monofilaments, mats, or tow, provide reinforcement for a metal matrix alloy. A transient liquid diffusion bonding agent, which may be a thin foil, a powder, or a coating, provides a vehicle for consolidating the fibers into the metal matrix. The reinforcing fibers and the bonding agent are placed between layers of the metal matrix and the whole structure is heated under minimal pressure to liquify the bonding agent. The liquid bonding agent infiltrates the fiber mat or tow to surround and wet each fiber and diffuses into and becomes alloyed with the matrix material, resulting in rapid isothermal solidification of the alloy and consolidation of the fibers in the matrix.

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TECHNICAL FIELD

The present invention relates to composite materials and, in particular, to fiber reinforced metal matrix composites synthesized by transient liquid consolidation.

BACKGROUND OF THE INVENTION

Composite materials can be designed with properties, such as toughness, high strength, and low weight, that are useful in many applications where homogeneous materials are less effective or inadequate. For example, fiber reinforced materials, a broad class of composites, typically comprise fibers of a material, such as glass or ceramic, that are embedded in a matrix material, such as plastic or metal, to improve the strength of the matrix material. Fabrication of such reinforced materials can often be difficult, however, because of physical incompatibilities between the fibers and the matrix material.

One method of fabricating multiple ply, continuous fiber reinforced metal matrix composites is the so-called foil/fiber/foil process. In this process, reinforcing fibers are sandwiched between layers of a metal foil. Pressure and heat are then applied to the layered structure for solid state consolidation of the fibers into the metal structure.

The basic foil/fiber/foil process, although adequate for consolidation of large diameter fibers in relatively soft metal matrices, has proven unsatisfactory for consolidation of small diameter, brittle fibers, especially in the form of tow, in relatively hard matrix alloys. For example, at the high temperatures, pressures, and exposure times required for consolidation with creep-resistant alloys or other matrix materials that resist diffusion bonding, the reinforcing fibers receive excessive chemical and mechanical damage during the process without being fully consolidated within the matrix. Thus, there is a need for new and effective methods of forming metal matrix composites with fully consolidated reinforcing fibers.

SUMMARY OF THE INVENTION

The present invention comprises a method of consolidating reinforcing fibers in metal matrix materials to form metal matrix composites. Small diameter brittle fibers, such as alumina (Al_2O_3) fibers, may be provided in the form of mats or tow and may include a suitable protective coating. A transient liquid diffusion bonding agent, such as silver (Ag), for example, which maybe in the form of a thin foil, a powder, or a coating, is provided as a vehicle for consolidating the fibers into the metal matrix material. The bonding agent is selected to have a melting temperature lower than that of the matrix material, good wetting of the fibers in its liquid phase with minimal reaction with the fibers (or fiber coating), high solubility and/or diffusivity in the matrix material, and rapid isothermal solidification when diluted with elements of the matrix material.

The reinforcing fibers and the transient liquid diffusion bonding agent are placed between layers of the metal matrix material to form a layered structure. The layered structure is then heated under minimal pressure to avoid damage to the fibers. Upon liquefaction, the bonding agent infiltrates the fiber mat or tow to surround and wet each fiber. At the same time, the liquid bonding agent diffuses into and becomes alloyed with the matrix material, resulting in rapid isothermal solidification and full consolidation of the fibers in the matrix. Thus, the transient liquid diffusion bonding agent infiltrates the reinforcing fibers, consolidates the fibers into the metal, and bonds the layers of matrix material.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the present invention and for further advantages thereof, the following Detailed Description of the Invention makes reference to the accompanying Drawings, in which FIGURES 1A-D are schematic cross sections illustrating the basic steps in synthesizing a metal matrix composite by transient liquid consolidation.

DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises a method of forming metal matrix composites in which reinforcing fibers are consolidated within the metal matrix. In general, the method is useful for consolidating fibers in metals that resist solid state diffusion bonding. The method is particularly useful for consolidating small diameter, brittle fibers, such as alumina fibers (Al_2O_3 in polycrystalline or single crystal form), in high-temperature, creep-resistant alloys, such as gamma titanium aluminide alloys (γ-TiAl) or Fe-Ni-Co superalloys.

The basic method of the present invention is illustrated schematically in Figures 1A-D. A metal matrix material 10, which is shown with a schematic representation of grain boundaries, is provided in layers such as foil sheets. Reinforcing fibers 12, which may be provided in the form of monofilaments, mats, or tow and which may include a protective coating, are sandwiched between layers of a transient liquid diffusion bonding agent 14. The fiber/bonding agent sandwich is in turn sandwiched between the layers of matrix ma-

terial 10. Although bonding agent 14 may be applied as a double (as illustrated in Figure 1A) or a single layer of foil, it may also be applied effectively in various other forms, such as a loose powder, a coating on fibers 12 or the bonding surfaces of matrix 10, or an impregnated layer in the surfaces of matrix 10.

When heated, transient liquid diffusion bonding agent 14 acts as a vehicle for consolidating fibers 12 within matrix 10 by infiltrating the fiber mat or tow, wetting the individual fibers 12, and then isothermally solidifying and diffusing into matrix 10 to bond the layers. For the fabrication of high quality metal matrix composites, it is desirable that transient liquid diffusion bonding agent 14 have the following properties:

1. A melting temperature less than the melting temperature of matrix 10;
2. Good infiltration and wetting of the fibers (or fiber coatings);
3. Minimal dissolution of or reaction with the fibers (or fiber coatings) to avoid degradation of fiber strength and/or formation of brittle interlayers;
4. Rapid isothermal solidification (i.e., steep rise in solidus and liquidus) when diluted with major matrix alloy elements;
5. High solubility and/or high diffusivity in the matrix alloy (i.e., rapid homogenization);
6. No equilibrium low melting temperature or brittle phases in the homogenized matrix; and
7. A desirable balance of properties in the homogenized matrix alloy.

After fibers 12 and transient liquid diffusion bonding agent 14 have been sandwiched between layers of metal matrix 10, the structure is heated under low pressure until bonding agent 14 liquifies. As shown in Figure 1B, liquified bonding agent 16 infiltrates the fiber tow and wets the individual fibers 12. Liquid bonding agent 16 also diffuses into and begins to dissolve the matrix material 10. The wetting of fibers 12 by liquified bonding agent 16 may be facilitated by the dissolution of active elements from matrix material 10. The process rapidly produces an isothermally solidified, heterogeneous metal matrix 18 around fibers 12, as illustrated in Figure 1C. Although the production of heterogeneous matrix 18 is essentially isothermal, the temperature and pressure may be varied after liquefaction of bonding agent 14 to achieve desired characteristics of matrix 18. The advantages of rapid, low pressure, essentially isothermal solidification of matrix 18 include full consolidation of and minimal damage to and/or reaction with fibers 12. Furthermore, the selection and use of transient liquid diffusion bonding agent 14 provides control of factors such as the effectiveness of fiber wetting, the bond strength, and the creep resistance of the metal matrix composite, for example. Finally, the structure may be subjected to a temperature/pressure treatment profile, if desired, to homogenize metal matrix 10 around fully consolidated fibers 12, as illustrated in Figure 1D.

PROCESS EXAMPLE: Gamma TiAl/Al_2O_3

Metal matrix composites comprising alumina (Al_2O_3) fibers in a gamma titanium aluminide (γ-TiAl) matrix have a high strength-to-weight ratio at temperatures up to about 980 °C. Alumina fibers, in single crystal (sapphire) or polycrystalline form, are useful for reinforcing high-temperature, creep-resistant metals because of their minimal chemical reactivity and good thermal expansion match with the metal matrix. In addition, polycrystalline alumina fibers having a nominal diameter of approximately 11 μm are available commercially from the 3M Company in the form of a 400-fiber tow.

In the γ-TiAl / Al_2O_3 system, silver (Ag) is a preferred metal to act as transient liquid diffusion bonding agent 14. Silver has a convenient melting temperature (962 °C) and a relatively high solubility (about 7% by weight) in both γ and α-2 phases of TiAl with negligible effect on the relative stabilities of the γ, α-2, and β phases of titanium. In addition, silver is relatively soft and compliant and may be applied as an interface material in several different forms, such as foil, powder, or coating, for example.

In one experiment, a tow of alumina fibers and a single layer of 38 μm Ag foil were placed between layers of matrix material cut from a powder-processed, Ti-48Al-2.5Nb-0.3Ta forged alloy. The layered structure was vacuum hot pressed at 1100 °C, 34 MPa, for one hour. The liquid silver was very effective in infiltrating the alumina fiber tow and aided in the natural spreading of the fibers along the interface of the two layers of matrix alloy during the hot pressing operation. In addition, X-ray energy dispersive microanalysis indicated that the silver had dispersed very well after isothermal solidification. No silver concentrations higher than 2% by weight could be found, even at the bond line, and silver was detected up to 600 μm from the bond line. Microhardness measurements found no soft regions either close to or distant from the bond line. However, a very hard region was found immediately adjacent to each Al_2O_3 fiber. Transmission electron microscopy diffraction analysis showed this region to have an α-2 crystal structure, which is consistent with the expected dissolution of alumina fibers by the liquid silver after sufficient titanium has dissolved in the liquid to attack the fiber surfaces.

The metal matrix composite produced by the foregoing process was subjected to 100 thermal

cycles from room temperature to 980 °C in a vacuum. The thermal cycling did not produce any microcracking around or between the fibers. Although this may indicate that the "reaction" layer of hard α-2 is acceptable for a useful composite, various steps have been evaluated for minimizing or eliminating the reaction. The easiest approach is to minimize the dwell time of liquid Ag-Ti on the fiber surfaces. This approach, with careful control of the temperature cycle, has proven somewhat effective in reducing the amount of α-2 phase material around the fibers. Another approach, which may be more effective, is to pre-coat the fibers with a thin layer of a suitable protective material. An ideal fiber coating material is one that can be applied conveniently as a thin layer and that survives exposure to the liquid (Ag-γ-Ti) with just enough reactivity to promote good fiber wetting, but which does not cause significant fiber degradation or the formation of detrimental matrix reaction layers. Various ceramic materials as well as refractory metals, such as niobium (Nb), molybdenum (Mo), tantalum (Ta), tungsten (W), and rhenium (Re), may provide effective fiber coatings. Of the coating materials evaluated, Y_2O_3 and Er_2O_3 were only moderately attacked by the liquid bonding agent, and TiB_2 was virtually unaffected. A coating of Mo was found to be effective in protecting Al_2O_3 fibers from the liquid bonding agent even though it reacted to form a new phase around the fibers. At the present time, TiB_2 and Mo are considered prime candidates for protective coatings for alumina fibers.

PROCESS EXAMPLE: Incoloy® 909/Al_2O_3

Incoloy® 909 is an iron-based superalloy having a low coefficient of thermal expansion and reasonably good resistance to high-temperature, high-pressure hydrogen embrittlement. Incoloy® 909 is a candidate for fiber reinforcement because fibers can compensate for the low creep resistance of the alloy at maximum operating temperatures.

In one experiment, alumina fiber tows were placed between layers of Incoloy® 909. A NIFLEX™ 77 braze foil (Ni-7Cr-3Fe-4.5Si-3.0B, 58 µm thick) was used as the transient liquid diffusion bonding agent 14. Boron (B) and silicon (Si) are the effective melting temperature depressants in this foil for the main superalloy elements of iron (Fe), nickel (Ni), and cobalt (Co). Using the transient liquid consolidation method of the present invention, complete consolidation of the fibers in the Incoloy® 909 matrix was achieved. There appeared to be no adverse reaction between the liquid metal and the fibers in forming this metal matrix composite. Elevated temperature exposures and thermal cycling of this composite produced no degradation (reaction or cracking) of either the fibers or the matrix interface region.

Alternatives to NIFLEX™ 77 foil as the transient liquid diffusion bonding agent 14 may be used to minimize the amount of liquid phase produced at the matrix interfaces and to minimize the modification of the matrix alloy composition. For example, a fine powder of the matrix alloy with sufficient boron and/or silicon added to depress the melting point (i.e., eutectic melting) to a practical consolidation temperature may be prepared by a number of conventional powder processing techniques, such as inert gas atomization. A thin layer of the powder can be applied to the bonding surfaces of the layers of matrix material using an alcohol carrier, for example. The fibers can then be placed between the powder-coated layers of matrix material, and the structure can be processed as described above. The powder can also be applied directly to the fiber monofilaments, mat, or tow. Conventional low-residue organic binder compounds may be used to hold the powder in place during handling of the fibers. A third alternative is to apply a melting point depressant, such as boron, directly to the bonding surfaces of the matrix material in the form of a coating, a powder, or a vapor impregnation of the matrix material.

The foregoing process examples describe the consolidation of alumina fibers in two significantly different matrix materials, but the process of the present invention is not limited to these specific types of reinforcing fibers or matrix materials. In addition to the titanium aluminide and superalloy materials described above, the matrix may comprise α-Ti, β-Ti, or $\alpha+\beta$-Ti alloys or other alloys of Fe, Ni, or Co, which generally require Cr, Ti, or Zr to form strong bonds with alumina fibers. The matrix may also comprise high strength aluminum alloys, where the process may be particularly useful for incorporating delicate fibers, such as embedded optical fibers. Suitable reinforcing fibers include Al_2O_3, TiB_2, and SiC (such as Textron SCS-6), for example, which may have protective coatings such as TiB_2, Y_2O_3, Er_2O_3, or refractory metal, for example. Suitable transient liquid diffusion bonding agents 14 include, for example, Ag, Cu, Al, and alloys such as Ti-Cu-Ni, Ag-Al, and Cu-Al for titanium-based matrix alloys; Zn, Mg, Zn-Al, and Mg-Al for aluminum-based matrix alloys; and B, Si, P, and alloys thereof as melting temperature depressants for Fe-Ni-Co superalloys.

As stated above, the transient liquid consolidation method of the present invention can be used with a variety of metal matrix composite systems. Manufacturing benefits include low pressure consolidation, use of high-strength creep-resistant matrix alloys, use of fiber mats or tow, and use of bonding agents in various forms such as foils,

powders, and coatings. The quality of metal matrix composites is improved because the process produces less fiber damage and fewer diffusion bonding defects such as voids, oxides, carbides, and intermetallic particles. In addition, the transient liquid consolidation process provides opportunity for control of fiber/matrix wetting, bond strength, and physical properties of the metal matrix composite.

Although the present invention has been described with respect to specific examples thereof, various changes and modifications may be suggested by this disclosure to one skilled in the art. Therefore, it is intended that the present invention encompass such changes and modifications as fall within the scope of the appended claims.

Claims

1. A method of forming a metal matrix composite comprising fibers (12) consolidated within a matrix of metallic material (10), characterized by the steps of:
   providing a transient liquid diffusion bonding agent (14);
   disposing the fibers (12) and said bonding agent (14) between layers of the matrix material (10) to form a layered structure;
   heating said layered structure to liquify said bonding agent (16);
   wetting the fibers (12) with said liquified bonding agent (16); and
   solidifying said bonding agent (18) to consolidate the fibers (12) in the matrix (10).

2. The method of Claim 1, wherein the step of solidifying said bonding agent further comprises the steps of:
   dissolving some of the matrix material (10) in said liquified bonding agent (16) to form a bonding alloy (18); and
   isothermally solidifying said bonding alloy (18).

3. The method of Claim 2, further comprising the step of diffusing said bonding alloy (18) to consolidate the fibers (12) in a homogeneous matrix (10).

4. The method of Claim 1, wherein the step of providing fibers (12) further comprises the step of providing a mat or tow of alumina fibers (12).

5. The method of Claim 4, further comprising the step of providing a titanium aluminide alloy as the matrix material (10).

6. The method of Claim 5, further comprising the step of coating said alumina fibers (12) with a protective coating selected from the group of materials consisting of Nb, Mo, Ta, W, Re, TiB_2, Y_2O_3, and Er_2O_3.

7. The method of Claim 5, wherein the step of providing a transient liquid diffusion bonding agent (14) comprises selecting said bonding agent (14) from the group of materials consisting of Ag, Cu, Al, and Ti-Cu-Ni, Ag-Al, and Cu-Al alloys.

8. The method of Claim 3, wherein the step of providing a transient liquid diffusion bonding agent (14) comprises providing said bonding agent (14) as a foil, a powder, or a coating.

9. The method of Claim 3, further comprising the step of providing a superalloy as the matrix material (10) and selecting said bonding agent (14) from the group of materials consisting of B, Si, P, and alloys thereof.

10. The method of Claim 3, further comprising the step of providing an aluminum alloy as the matrix material (10) and selecting said bonding agent (14) from the group of materials consisting of Zn, Mg, Zn-Al, and Mg-Al.

11. A method of forming a metal matrix composite comprising a mat or tow of small diameter, brittle fibers (12) consolidated within a matrix of metallic material (10), characterized by the steps of:
    providing a transient liquid diffusion bonding agent (14);
    disposing the fibers (12) and said bonding agent (14) between layers of the matrix material (10) to form a layered structure;
    heating said layered structure to liquify said bonding agent (16);
    infiltrating the mat or tow and wetting the fibers (12) with said liquified bonding agent (16); and
    isothermally solidifying and then diffusing said bonding agent (18) to consolidate the fibers (12) in the matrix material (10).

12. The method of Claim 11, wherein the step of providing a matrix of metallic material (10) comprises providing a matrix of material (10) selected from the group consisting of titanium alloys, titanium aluminide alloys, aluminum alloys, and Fe-Ni-Co superalloys.

13. The method of Claim 12, wherein the step of providing a mat or tow of fibers (12) comprises providing a mat or tow of Al_2O_3 reinforcing

fibers (12).

14. The method of Claim 13, wherein the step of providing a transient liquid diffusion bonding agent (14) comprises providing said bonding agent (14) in the form of a foil, a powder, or a coating.

15. The method of Claim 13, wherein the step of providing a mat or tow of Al_2O_3 fibers (12) comprises providing Al_2O_3 fibers (12) having a coating selected from the group of materials consisting of Nb, Mo, Ta, W, Re, TiB_2, Y_2O_3, and Er_2O_3.

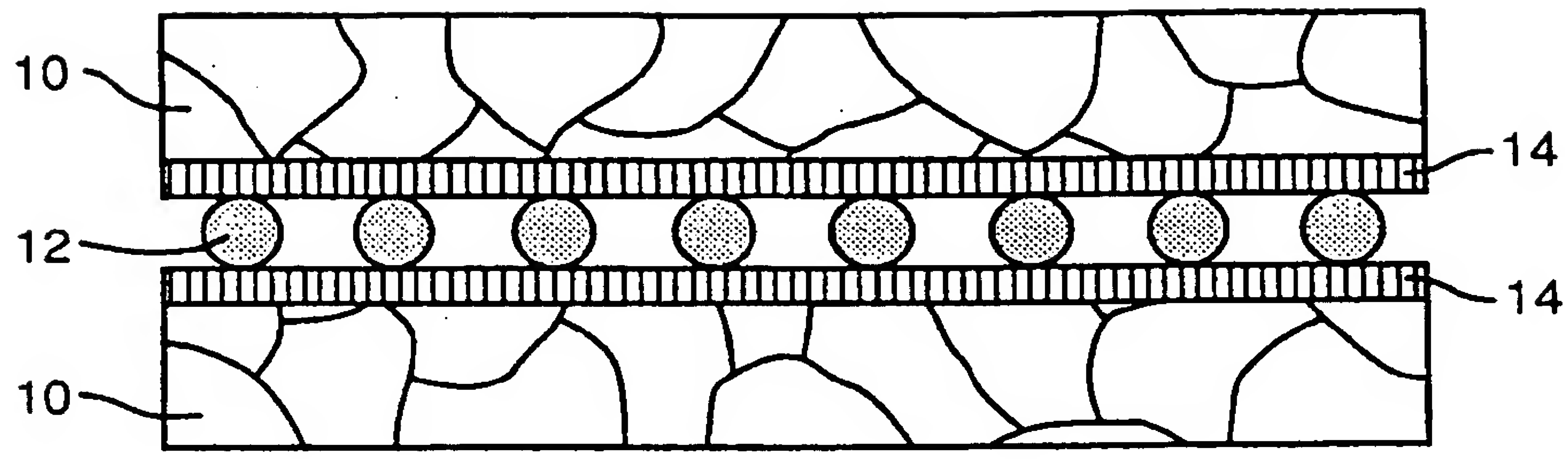

Figure 1A

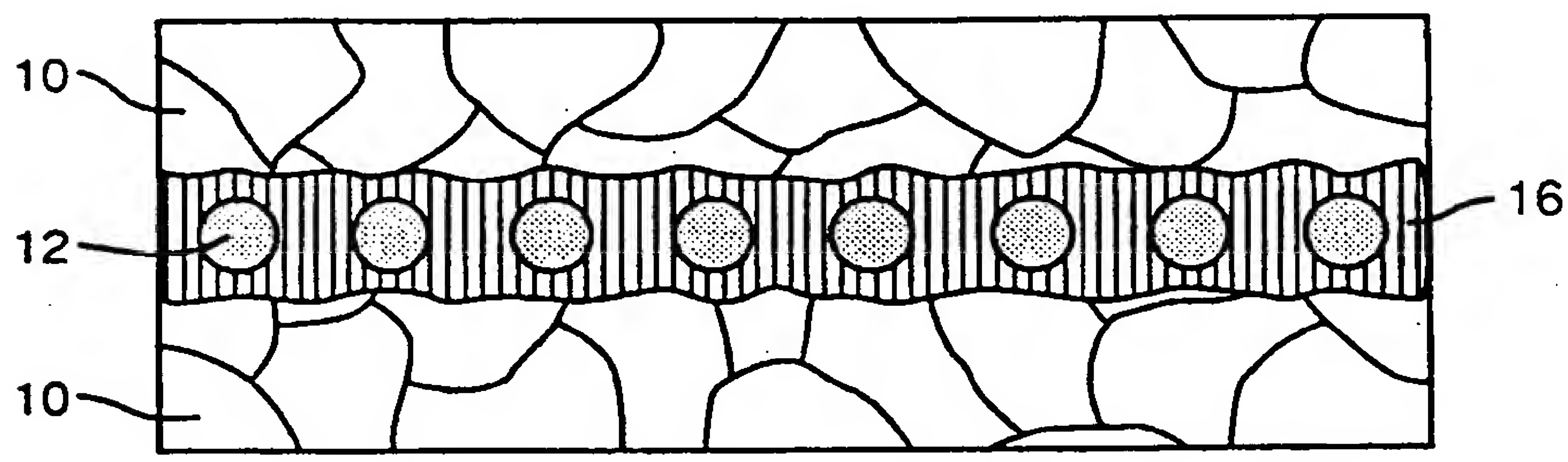

Figure 1B

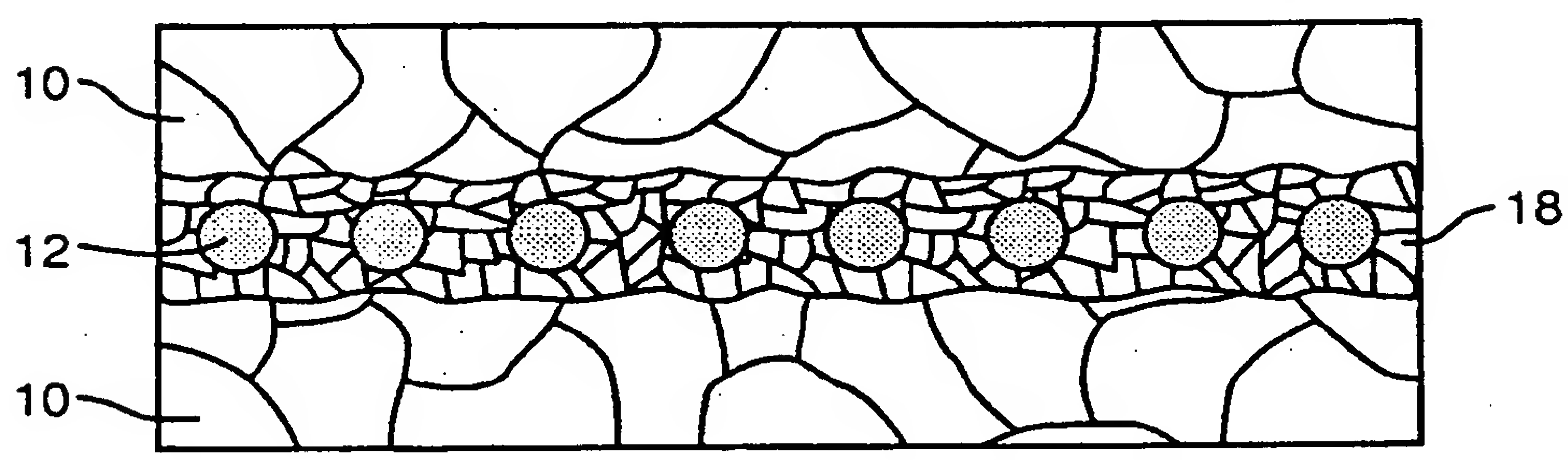

Figure 1C

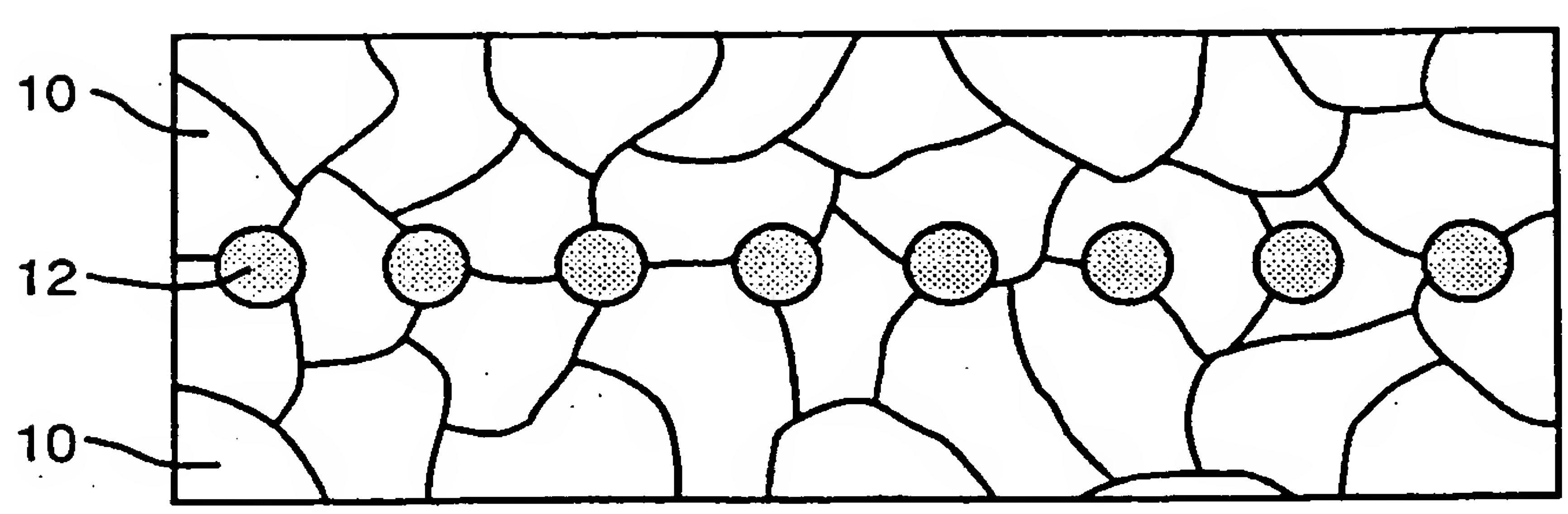

Figure 1D

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 10 3385

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X Y	US-A-4 847 044 (A.K.GHOSH) * claims 1-7; examples 2,4 *	1-5,8,10 7,9	C22C1/09 B23K35/00
X Y	US-A-3 936 277 (J.M.JAKWAY) * claim 1 *	1-3,8 7	
Y	US-A-3 678 570 (D.F.PAULONIS ET AL) * claim 1 *	9	
A	EP-A-0 121 209 (ROCKWELL INTERNATIONAL CORP) * claim 23 *	1-10	
A	EP-A-0 334 505 (TEXAS INSTRUMENTS INC) * claims 25,27 *	1-10	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C22C
B23K

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23 JUNE 1992	SCHRUERS H.J.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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